

A RISK-BASED LIFE CYCLE ASSESSMENT OF OPAL
PETROL AND BP REGULAR UNLEADED PETROL

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A Risk-based Life Cycle Assessment of OPAL Petrol and BP Regular Unleaded Petrol

by

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Abstracts

Gasoline sniffing has been a significant health issue in remote communities in many countries, such as Labrador in Canada. In order to reduce the adverse impacts caused by gasoline sniffing on human health, a new less toxic blend of gasoline (OPAL) produced by BP Australia is proposed to be introduced. This study focuses on the estimation of impacts and risks of OPAL on human health and the environment and its comparison to BP regular unleaded petrol (ULP). A risk-based life cycle analysis was conducted. The results show that OPAL is identified to have less adverse impacts on both the environment and human health. In addition, the risks to human health by using OPAL can be regarded as negligible. Moreover, compared to ULP, OPAL proved to have less risk to human health both in carcinogenic and non-carcinogenic categories. Therefore, it can be predicted that the introduction of OPAL would significantly help to reduce the harmful effects caused by gasoline sniffing in remote areas.

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Acronyms and Abbreviations

AULPIH	American Conference of Governmental Industrial Hygienists
BTX	Benzene, Toluene, Xylene
CNC	Central Nervous System
CRC	Comparative Risk Assessment
EIRA	Environmental Impact and Risk Assessment
GHG	Greenhouse Gas
GWP	Global Warming Potential
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LPG	Liquefied Petroleum Gas
MCL	Maximum Contaminant Level
NIOSH	National Institute for Occupational Safety and Health
NOAEL	No Observable Adverse Effect Level
OPAL	OPAL Petrol
OSHA	Occupational Safety and Health Administration
PEL	Permissible Exposure Limit
PEMFC	Proton Exchange Membrane Fuel Cell
PRA	Probabilistic Risk Assessment
RA	Risk Assessment
RBLCA	Risk-based Life Cycle Assessment
RfC	Reference Concentration
RME	Rape Methyl Eater
RON	Research Octane Number
RVP	Reid Vapour Pressure
SF	Carcinogen Slope Factor
SI	Spark Ignition
THC	Total Hydrocarbons
ULP	BP Regular Unleaded Petrol
USEPA	U.S. Environmental Protection Agency
VOCs	Volatile Organic Compounds

Chapter 1 Introduction

1.1 Background information

Gasoline is the fuel used in cars, other small vehicles, and light aircraft that are powered by spark ignition (SI) engines. It consists mostly of aliphatic hydrocarbons. Iso-octane or the aromatic hydrocarbons (toluene and benzene) are added to increase its octane rating (Lucas, 2001). However, gasoline sniffing has been an important health concern in remote communities in many countries. The health effects associated with gasoline sniffing are numerous: cancer, leukemia, heart attack, brain damage, and even death (Brown, 2007). The toxicity of gasoline is mainly attributed to the presence of mono-aromatic hydrocarbons (BTX-benzene, toluene, ethyl-benzene, and xylenes) (Paixao et al., 2006). In order to reduce the adverse impacts of gasoline sniffing on human health, a new less toxic blend of gasoline by the name of OPAL petrol (OPAL) was produced by BP in Australia. OPAL is a hydrocarbon fuel, which has very low levels of compounds such as benzene, toluene and xylene (typically less than 5% volume). These compounds are believed to be associated with the narcotic effects from sniffing gasoline. In addition, OPAL also has very low levels of sulphur, less than 10 ppm and meets the highest standard for petrol for modern vehicles (BP, 2006). Furthermore, OPAL proved to be effective in reducing the harm of gasoline sniffing in Australia through the Petro Sniffing Prevention Program which was implemented in over 100 sites in Australia by the Australian Government (Brown, 2007).

1.2 Research Problem Description

Since gasoline sniffing is also a serious problem in remote communities in Labrador, the Genesis Group, in corporation with Innu Nation, Nunatsiut Government, Health Canada, and Memorial University, decided to examine the feasibility of the application of OPAL in Labrador and, by extension, other parts of the Canadian North. However, no study was found to show the impacts and risks caused by OPAL. Therefore, this study focuses on the estimation of the impacts and risks of OPAL on human health and the environment, and its comparison to the BP regular unleaded petrol (ULP) which is widely used in Australia now in order to delineate the benefits of OPAL.

The objective of this study:

- Conduct a detailed Risk-based Life Cycle Assessment (RBLCA) of OPAL and compare with ULP.

1.3 Overview of thesis

The whole thesis consists of six chapters, which are introduction, literature review, methodology, application of RBLCA to OPAL and ULP, discussions, and conclusions.

In Chapter 1, the reason for conducting this study is first introduced. The impact to human health and environment caused by OPAL is compared to ULP from life cycle and risk perspectives in order to delineate the benefits of OPAL. This study provides a clear picture of OPAL's performance on human health and the environment, which can assist significantly in decision making and the selection of the best available alternatives.

In Chapter 2, the background information of OPAL and ULP is introduced, and the typical characteristics are also compared. In addition, previous measurements and assessments of OPAL are summarized. It is known that no similar study has been conducted yet, which emphasize the originality of the study. In addition, the advantages of RBLCA compared to conventional life cycle assessment (LCA) are also described.

In Chapter 3, a detailed description of the methodology, RBLCA, used in this study is introduced. RBLCA mainly contains two parts: conventional life cycle assessment and risk assessment. The primary steps are: defining the goal and scope of the study, inventory analysis, impact assessment, and risk assessment.

In Chapter 4, RBLCA is applied to OPAL and ULP in order to compare which one has less adverse impacts and risks on human health and the environment. The results show

that OPAL has less adverse impacts and risks on both human health and the environment than ULP. An uncertainty analysis is also conducted to prove the validity of the results.

In Chapter 5, discussions based on the results obtained in Chapter 4 are conducted. Additionally, because of a lack of information and data, the study has several limitations. These limitations are also discussed in this chapter.

In Chapter 6, the final conclusions of the present work and some recommendations for the future work are presented.

Chapter 2 Literature Review

2.1 OPAL and ULP

OPAL is a hydrocarbon fuel for use in spark ignition engines. It has a characteristic sweet smell readily identified as gasoline and is distinct from the more pungent smell of regular unleaded gasoline (BP, 2009). OPAL is a complex mixture of volatile hydrocarbons containing paraffins, naphthenes, olefins and aromatics with carbon numbers predominantly between C4 and C12. It may also contain oxygenates and small quantities of proprietary performance additives (BP, 2009). According to its specifications, OPAL is identified as a regular grade 1 gasoline, vapour pressure class 3, and distillation class A according to the Canadian standards for unleaded automotive gasoline. OPAL is blended from only three components: 75~80% alkylate, 20% isomerate, and the remainder butane.

OPAL is produced at the BP Refinery Kwinana in Western Australia (BP, 2006). In the BP refinery, Hydrogen recycle UOP Penex Process is applied in the isomerization unit. Through this process, octane boost from 65 to 84 Research Octane Number (RON) and removes benzene as a side reaction. In the isomerization unit, normal butane (C4) is converted to iso-butane for Alkylation, and normal pentane (C5) and hexane (C6) are converted to their respective isoparaffins for blending into gasoline to increase octane. The purpose of the alkylation process in BP refinery is to convert liquefied petroleum gas (LPG) to low Reid Vapour Pressure (RVP) clean burning gasoline. The alkylation

process for motor fuel production catalytically combines olefins with isobutane to form branched-chain isoparaffins of high octane number (Lucas, 2001). Finally, butane is the streams that arise from crude oil fractionation, and also include the saturated light hydrocarbons produced by cracking in the catalytic reformer and the distillate hydrocracker (Lucas, 2001).

In this paper, ULP is selected to be compared with OPAL because it is also produced by BP Australia. Moreover, OPAL has similar specifications to ULP (SWB Consulting, 2007). Similarly, ULP is a complex mixture of volatile hydrocarbons containing paraffins, naphthenes, olefins, and aromatics with carbon numbers predominantly C_4 and C_{12} . It may also contain oxygenates and small quantities of proprietary performance additives (BP, 2009). Since, the information of ULP blending has not been found yet, it is hard to identify the refining processes of ULP.

For one of the purposes of the study is to estimate the risk of OPAL and ULP to human health, it is essential to know the contents of those hazardous components in both types of the gasoline. Based on the information which can be found, a general comparison of composition between OPAL and ULP was summarized in Table 1.

Table 1 Typical characteristics of OPAL and ULP (BP, 2009)

PROPERTY	UNITS	OPAL	ULP
Lead	g/L	<0.005	<0.005
Oxygenates MTBE DIPE TBA ethanol	%vol	<0.2 <0.2 <0.2 <0.2	Data cannot be found
Sulfur	ppm	<10	100
Benzene	%vol	<1	<1
Toluene+Xylene	%vol	<5	25
Aromatics	%vol	<5	42max
Olefin Content	%vol	<3	25

According to the data in Table 1, the lead content and benzene content in OPAL and ULP are the same. However, it is obvious that OPAL and ULP have differences in composition. Generally, small amount of aromatics occur naturally in blends of gasoline. In addition, aromatic rich streams containing these hydrocarbons are added as blending agents in percent concentrations to unleaded gasoline to improve the antiknock characteristics of gasoline. Aromatics are known to be very harmful to human health (Reese & Kimbrough, 1998). OPAL has less than 5 vol% aromatics, which is much less than that in ULP. As a carcinogen, the content of benzene is strictly controlled. According to the data in Table 1, the benzene content of both types of gasoline is less than 1 vol%. Besides, toluene and xylene are also specially concentrated because of their high toxicity. From Table 1, it is known that ULP has 25 vol% toluene and xylene, while OPAL only contains less than 5 vol%. Sulphur is controlled in the finished gasoline to limit emissions of sulphur oxides (SO_x) and the odour of certain sulphur compounds, and

to enhance storage stability (Lucas, 2000). From Table 1, OPAL contains less than 10 ppm sulphur, while the sulphur content in ULP is 100 ppm.

2.2 Commercial Testing

In 2005, OPAL was developed by BP in partnership with the Federal and Northern Territory Governments, Indigenous communities and educational bodies. Since then, several tests and comparisons with ULP have been conducted including:

- i. In 2004, BP commissioned Toyota to perform testing on the tail pipe exhaust emissions (hydrocarbons, carbon monoxide, and nitric oxide) and the driveability of OPAL on three cars. The methodology used for this testing followed the Australian Design Rules for emissions testing. Results of this testing showed that there was no significant difference in driveability performance when a vehicle runs on OPAL compared to the same vehicle running on ULP. In addition, the tail pipe emission discharged by the vehicle using OPAL is less than that using ULP.
- ii. In February 2005, BP commissioned Orbital Engineering Service (OES) to undertake an assessment of a Yamaha 150 hp four stroke outboard operating on OPAL and ULP, and a study on the impact on the performance of a marine outboard two stroke engine. The results showed that the performance of the engine on both fuels could not be differentiated with the exception of startability following a tank run dry simulation.

iii. In 2006, BP commissioned OES to undertake further testing on vehicle driveability/performance, fuel economy and fuel emissions. The methodology used for this testing included:

- Driveability assessments, where the vehicle driveability was evaluated by means of an open road test, based on industry standards, and its wide open throttle performance was tested using a chassis dynamometer;
- Fuel economy testing conducted to the ADR37/01 and AS 2877 standards for emissions and fuel consumption determination; and
- Engine performance was tested by the vehicle being driven on the emissions chassis dynamometer at wide open throttle at fixed vehicle speeds of 80,90 and 100 km/h in second gear, recording both the power absorbed at the wheels by the chassis dynamometer and engine revolutions per minute (rpm).

The results of the testing confirmed that OPAL, compared to ULP, had little driveability difference, a slight reduction in vehicle emissions, and higher fuel consumption by 2-3% as a direct result of richer combustion mixtures (SWB Consulting, 2007; BP, 2006).

Although some of the testing measured the tail pipe emission discharged by the vehicles running on OPAL, no study specifically focused on the estimation of adverse impacts and risks caused by OPAL to human health and the environment was found. Therefore, it is

necessary to conduct a study to estimate the OPAL's potential effects and risks on human health and the environment, and to compare it to ULP in order to delineate the benefits of OPAL.

2.3 LCA

LCA development began in the late 1960s with a technique designed to analyze resource utilization. LCA development first accelerated during the energy crises of the 1970s, and again for a short period in the late 1980s and early 1990s, with attempts to use LCA for environmental marketing claims (Owens, 1997). Now, LCA is a widely used method to estimate the potential environmental impacts of products or systems. It is a conceptual frame work and methodology for the assessment of environmental impacts and human health effects of product systems on a cradle-to-grave basis. The LCA approach is a departure from conventional assessments which tend to focus either on product manufacturing or end-of-life disposal. An analysis of a system under LCA encompasses the extraction of raw materials and energy resources from the environment, the conversion of these resources into the desired product, the utilization of the product by the consumer, and finally the disposal, reuse, or recycling of the product after its service life. The LCA approach is an effective way to introduce environmental considerations in process and product design or selection (Azapagic, 1999).

LCA has been successfully applied to quantify the health and environmental impacts of products throughout their life-cycles in many fields. The advantages of LCA have been cited by many researchers and their benefits are simply listed here (Owens, 1997; Sleeswijk et al., 2003; Bare, 2006).

- LCA is comprehensive in covering a large number of impacts. Impact categories include not only human toxicity and ecotoxicity, but also a large number of other impact categories, ranging from resource depletion to climate change.
- LCA is comprehensive in covering a large number of stressors, and locations. This fact will affect the manner in which LCA is conducted in many ways, including the level of spatial and temporal detail that is included within the modeling.

Although LCA has covered a wide range of applications, it has limitations. Many authors have studied the limitations of LCA, which are summarized by Bare (2006):

- There is no consensus on what should be included within LCA: the treatment of impact categories (e.g., human health), or the stressors that should be included within a LCA.
- LCA may not consider the temporal and spatial detail necessary to conduct scientifically defensible analyses (e.g., background concentrations, thresholds, stack heights, emission release timing). Although global impacts on a longer term scale (e.g., global warming potentials and stratospheric ozone potentials) are

easier to characterize with less spatial and temporal details (and thus are much easier to reach global consensus), categories that require additional temporal and spatial detail (e.g., smog formation) often must be specially developed with the spatial and temporal details necessary for the region and situation.

- For some impact categories, it is difficult to include issues of severity and/or potency in a manner that is consistent for all stressors within the impact category.
- Uncertainty is not completely characterized. Allocation based on a functional unit is dependent on the terms of reference, allocation method, and functional unit chosen.
- For aggregation of impacts and/or impact categories, weighting will be involved.

2.3.1 LCA applied to fuel

LCA is also a method commonly used to compare the potential environmental and human health effects of various types of fuels. In the past, considerable tests have been conducted by using LCA. Tan and Culaba (2001) conducted a LCA of several conventional and alternative motor vehicle fuels to find the most environmental friendly automobile fuel. Furuholt (1995) implemented LCA to compare the production and use of three different fuel emissions through the production chain, and assessed the potential impacts to the environment. Kaltschmitt et al. (1997) presented a study of conducting a LCA case study of Rape Methyl Ester (RME) compared with diesel fuel. Lave et al. (2000) also demonstrated a successful application of LCA to analyze fossil fuels

(conventional unleaded and reformulated gasoline, low sulphur reformulated diesel, and compressed natural gas), ethanol from biomass, and electricity together with current and advanced internal combustion engines and electric vehicles. Mata et al. (2003) published a study which compared the potential environmental impacts due to evaporative and leak emissions from several gasoline blends composed of reformat, alkylate, cracked gasoline, while using the Research Octane Number (RON) and Reid Vapour Pressure (RVP) criteria as constraints on the various acceptable gasoline blends. Through implementation of LCA, this study successfully estimated the different environmental impacts of three different gasoline blending options and provided valuable suggestions in selection of gasoline blending options. Granovskii et al. (2006) presented a LCA case study to compare hydrogen-fuelled proton exchange membrane fuel cell (PEMFC) vehicles to traditional internal combustion engine vehicles operating on gasoline.

These limitations may make LCA incorrectly predict actual effects, quantitate risks, or address safety issues. In addition, the role of LCA is only to compare two or more options to determine which is more environmentally friendly, therefore, it does not address risk, safety, or actual effects (Bare, 2006; Owens, 1997). Therefore, LCA cannot give a full report of the risks caused by a product life-cycle. However, the role of risk assessment (RA) is to identify and quantify the risks that result from the release of chemicals to the environment, and the resulting exposure of humans and ecosystem (Sleeswijk et al.,

2003). Therefore, LCA can be used in conjunction with RA, because together they provide important perspectives on environmental issues and human health.

2.5 Risk assessment

Risk assessments are used to determine if a particular chemical poses a significant risk to human health and environment, and if so, under what circumstances (Simeonov & Hassanien, 2008). Risk assessment is a system analytical tool to organize, structure and compile scientific information in order to help identify existing hazardous situations, anticipate potential problems, establish priorities and provide a basis for regulatory controls and/or corrective actions. A key underlying principle of risk assessment is that some risks are tolerable – a reasonable view, considering the fact that nothing is wholly safe (Flemstrom, Carlson, & Erixon, 2004). The USEPA first published a set of risk assessment guidelines (including carcinogen guidelines) in 1986 (Bare, 2006). Now, several types of RA have been developed for different purposes. Comparative risk assessment (CRA) has become an increasingly accepted research tool, and has helped to characterize environmental profiles and priorities (Andrews, Apul, & Linkov, 2006). The purpose of most comparative risk assessments is to identify the most important health risks from the point of view of the people affected (“Comparative risk assessment”, 1998). The micro applications of CRA are based on the analysis and evaluation of a relatively focused environmental problem. The goal of CRA in micro applications is to compare the risks of alternative solutions to a particular problem. This approach to problem solving

and decision making allows consideration of all possible options and preferably incorporation of stakeholder input into the decision making process. Micro applications of CRA consider multi-risks facing the society by comparing different types of environmental problems (Andrews, Apul, & Linkov, 2006).

Probabilistic risk assessment (PRA) is another widely used type of risk assessment, and is a systematic procedure for investigating how complex systems are built and operated. PRA models how human, software and hardware elements of the system interact with each other. Also, it assesses the most significant contributors to the risks of the system, and determines the value of the risk. PRA involves an estimation of the degree or probability of loss. The PRA procedure involves the quantitative application of the above triplets in which probabilities (or frequencies) of scenarios of events leading to exposure of hazards are estimated, and the corresponding magnitude of health, safety, environmental and economic consequences for each scenario are predicted. The risk value of each scenario is often measured as the product of the scenario frequency and its consequences. The main result of the PRA is not the actual value of the risk computed; rather it is the determination of the risks of that system, uncertainties associated with such estimates, and the effectiveness of various risk reduction strategies available. That is, the primary value of a PRA is to highlight the system design and operational deficiencies and optimize the resources that can be invested on improving the design and operation of the system (Modarres, 2008).

2.6 Integration of LCA and RA

The potential for the integration of RA and LCA has become of new interest to researchers. Owens (1997) compared LCA and RA to recognize the inherent differences and commonalities in them, and concluded that LCA impact assessment does not predict or measure actual effects, quantitate risks, or address safety because LCA loses spatial, temporal, dose-response, and threshold information. However, Owens also illustrated that LCA provides insights into hidden trade-offs and media shifts that are potentially valuable to risk assessors and managers. This suggests that opportunities may exist to use LCA results in a risk assessment.

Assies (1998) suggested an approach to life cycle impact assessment which is similar to, and compatible with, procedures for non-probabilistic risk assessment. The method is based on a comparison of predicted exploitation or exposure levels with critical levels. According to the results from the survey of the feasibility of the approach, it was concluded that life cycle risk assessment may contribute to a better harmonization of methods for impact assessment.

Sleeswijk et al. (2003) conducted an overview of LCA and RA differences from their goal and output, areas of applications, general procedures, and the nature of their

characteristics. Through comparison, the authors concluded the study with a proposal for the integration of LCA and RA into a common tool that combines them without the loss of their individual advantages. However, the authors also mentioned that a full integration of two tools is impossible for there exists a fundamental difference between LCA and RA. Therefore, it is essential to combine these tools properly. Bare (2006) proposed a coordinated approach for conducting LCA and RA using models consistent with the U.S. Environmental Protection Agency's (USEPA) handbooks, policies, and guidelines. In the study, two tools are chosen as examples to illustrate how LCA and RA can be used in combination. Bare concluded neither one should be used in isolation, but that combining the LCA and RA methodology are necessary to have a balanced perspective, since it is easier to see the complete environmental picture.

The methodology combining LCA and RA has been applied to real cases in many fields. Nishioka et al. (2002) used the methodology, integrating RA and LCA concepts, to preliminarily determine the magnitude and distribution of health benefits associated with increased residential insulation in new housing. Socolof and Geibig (2006) presented the complementary roles of LCA and RA, and successfully applied the combined methodology to a real case. In this methodology, a thorough LCA was conducted first, so that impact categories could be evaluated in the LCA, including human toxicity. Based on the LCA results, the process causing the most adverse impacts on human and

environmental toxicity should be identified. Then a detailed RA was applied to that process to assist in better understanding the potential for health and environmental risks.

In this study, a risk-based life-cycle assessment (RBLCA) was applied to estimate the potential adverse impacts and risks caused by OPAL to human health and the environment, and its comparison to ULP. A conventional IA was conducted to evaluate the impacts on human health and the ecosystem by using OPAL first. Since OPAL was introduced to reduce the harmful effects to human health from gasoline sniffing, a detailed human health risk assessment was applied to assess the potential risks to human by using OPAL. The same procedures were also applied to ULP, so that the results from two assessments can be compared. This study provided a clear picture to show the benefits on human health and the environment of OPAL compared to ULP, which offered a great support for decision-makers to decide whether they are going to introduce OPAL to remote areas, such as Labrador, even other places in the Canadian North. A detailed description of the methodology is presented in the subsequent chapters.

Chapter 3 Methodology

The methodology used in this study is the Risk Based Life Cycle Assessment (RBLCA) which is a process of weighting policy alternatives and selecting the most appropriate action by integrating the environmental risk assessment with social, economic, and political attributes to reach a decision. It identifies the options for the improvement of environmental performance and considers the material and energy supply chains within the system boundary (Sadiq & Khan, 2006). RBLCA mainly comprises two main steps: LCA, and RA. These two steps further consist of many sub-steps. The RBLCA framework is divided into three main phases: defining goal and scope, life cycle inventory analysis, and impact and risk assessment.

3.1 Defining goal and scope

The goal definition component states the reason for performing a specific study, defines the options that will be compared and the intended use of the results. This stage also involves identifying the system boundaries and the procedures for handling the data. Rules and assumptions must be documented (McDougall et al., 2001).

The scope of a study basically outlines the parameters within which the study will be carried out. These need to be compatible with the goals of the study. According to the

ISO 14040 requirements, the following information need to be clearly described: the functions of the product system(s), the functional unit, the system boundary to be studied, allocation procedures, the types of indicators and the methodology of Life Cycle Impact and Risk Assessment and subsequent Life Cycle Interpretation to be used, data requirements, assumptions, limitations, the initial data quality requirements, the type of critical review (if any) and the type and format of the report required for the study (McDougall et al., 2001).

3.2 Inventory analysis

This stage collects all the energy and material inputs, wastes and emissions data and quantifies the environmental load (Khan et al., 2005). Life Cycle Inventory (LCI) analysis should be comprehensive enough to make the final decision, but in instances where rough estimates have to be made, they must be conservative and clearly noted. In order to ensure the data used are in the best available form and the sources are contemporary, an extreme care must be taken (Sadiq & Khan, 2006). According to the ISO14041, a general flowchart of LCI is generated in Figure 1:

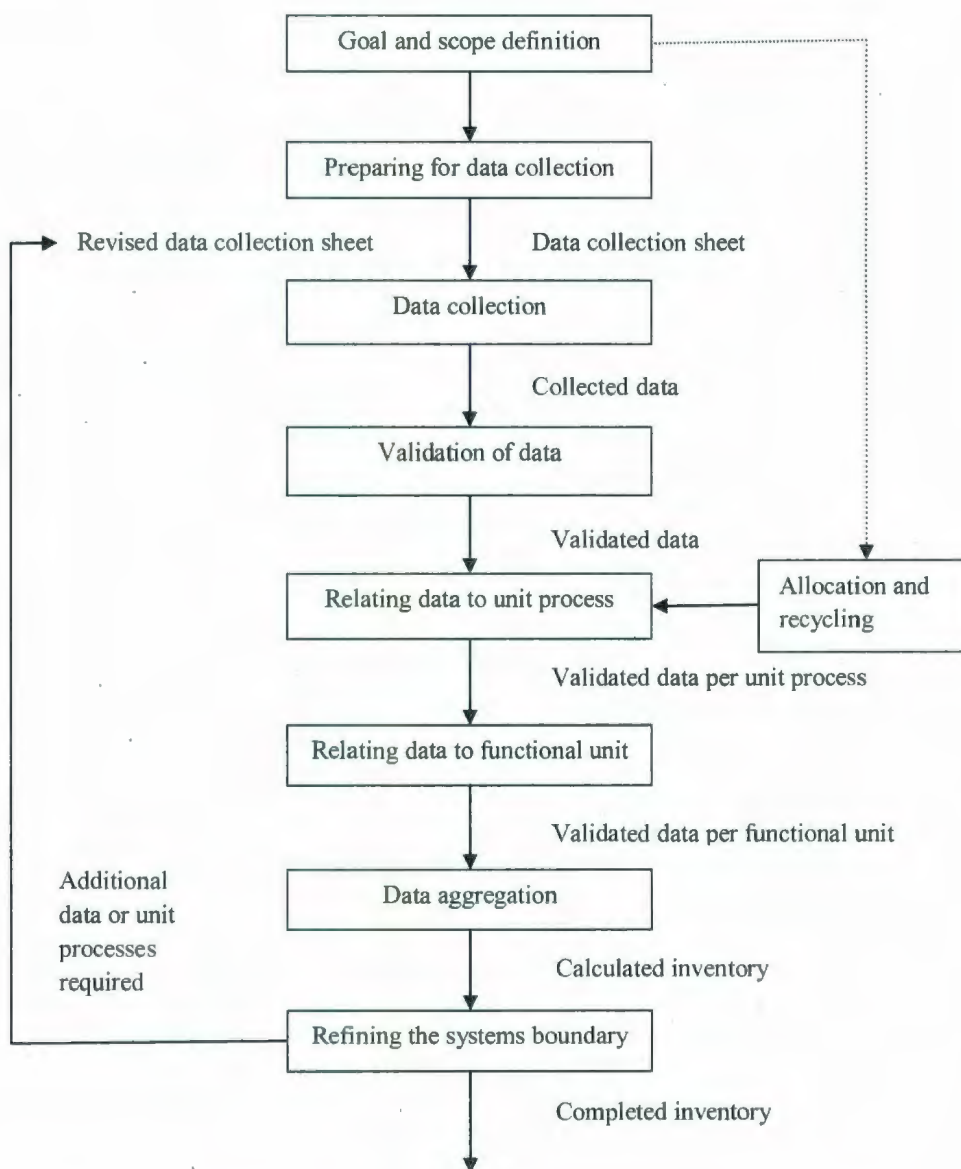


Figure 1 Flowchart of life cycle impact analysis (McDougall & White, 2001)

3.3 Impact and risk assessment

3.3.1 Impact assessment

Environmental impact and risk assessment (EIRA) examines the potential and actual environmental and human health effects from the use of resources (energy and materials) and environmental releases (Sadiq & Khan, 2006). An impact assessment is divided into two phases: classification, characterization, and interpretation (Khan, Hawboldt, & Iqbal, 2005). In this study, the Eco-indicator 99 methodology is used to calculate the damage scores of each component in the impact assessment. The Eco-indicator 99 impact assessment methodology, a damage oriented method for life cycle impact assessment, can be divided into three steps:

- i. Inventory of all relevant emission, resource extractions and land-use in all processes that form the life cycle of a product. This is standard procedure in LCA;
- ii. Calculation of the damages of these flows caused to human health, ecosystem quality and resources;
- iii. Weighting of these three damage categories (Geodkoop & Spriensma, 2001).

This three-stage method is represented in the Figure 2:

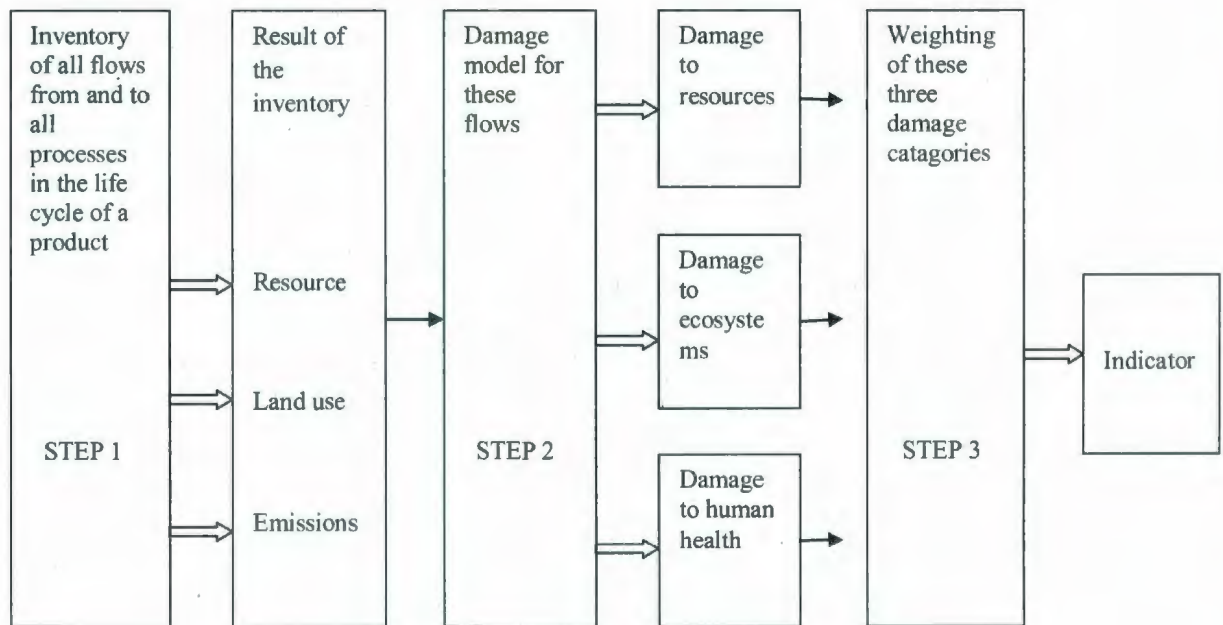


Figure 2 General procedure for the calculation of Eco-indicators (Geodkoop & Spriensma, 2001)

The classification stage requires the identification of inventory data relevant to each specific impact category and assignment of the appropriate LCI results to each category. Data may belong to more than one category (McDougall & White, 2001).

The characterisation phase requires calculations to be made to evaluate the relative significance of each contributor to the overall impact of the system or operation being studied, by converting these to a common indicator. The most critical and controversial step in characterization is the weighting step. Traditionally in LCA, the emissions and resource extractions are expressed as 10 or more different impact categories, like acidification, ozone layer depletion, ecotoxicity and resource extraction. For experts or non-experts it is very difficult to give meaningful weighting factors for such a large number and rather abstract impact categories. The problem is that experts cannot really grasp the seriousness of these impact categories, without knowing what effects are associated with them. Additionally, 10 is a relative high number of items to be weighted.

The Eco-indicator 99 methodology developed a weighting procedure not focusing on weighting the impact categories but the different types of damage that are caused by these impact categories. It reduces the number of items that are to be assessed to three, which are:

- i. Damage to Human Health, expressed as the number of year life lost and the number of years lived disabled.
- ii. Damage to Ecosystem Quality, express as the loss of species over a certain area, during a certain time.
- iii. Damage to Resources, expressed as the surplus energy needed for future extractions of minerals and fossil fuels.

The Eco-indicator 99 lists damage factors for the substance lists that can be found in most popular LCA database. Damage factors in the hierarchist perspective were used in this case. The weights in this case are specified below:

Table 2 The weights of damage factors in the hierarchist perspective (Geodkoop & Spriensma, 2001)

	Weights
Human Health	400
Ecosystem Quality	400
Resources	200

The weighted damages are calculated as the following equation:

$$\text{Weighted Damage} = \text{Mass of Emission} \times \text{Weighted Damage Factor} \quad \text{Equation 3.1}$$

The interpretation involves a review of all the stages in the previous process and a check that all assumptions are consistent. Three elements are needed to be identified during this stage: 1) Identify the significant issues based on the inventory analysis and impact assessment; 2) Evaluate the significant issues based upon completeness, sensitivity and consistency checks; 3) Draw conclusion, make recommendations and report the significant issues (McDougall & White, 2001).

3.3.2 RA

The goal of introducing OPAL to Canada is to reduce the adverse impacts on human health caused by gasoline sniffing, therefore, it is necessary to estimate the risk of OPAL to human health, then its comparison to ULP. Since LCA cannot identify the actual risk of OPAL, RA is applied to this study too. The risk assessment methodology, developed by U.S. Environmental Protection Agency (US EPA), is used to investigate human health risk in this study. Human health risk assessment includes four basic steps: hazard identification, dose-response assessment, exposure assessment, and risk characterization (US EPA, 2009).

Hazard identification is to identify the types of adverse health effects that can be caused by exposure to some agent in question, and to characterize the quality and weight of evidence supporting this identification. The key components of hazard identification are toxicokinetics and toxicodynamics. Toxicokinetics considers how the body absorbs, distributes, metabolizes, and eliminates specific chemicals. Toxicodynamics focus on the effects that chemicals have on the human body (USEPA, 2009).

Dose-response assessment is to document the relationship between dose and toxic effects. A dose-response relationship describes how the likelihood and severity of adverse health effects (the responses) are related to the amount and condition of exposure to an agent (the dose provided). Dose-response assessment is a two-step process. The first step is an

assessment of all data that are available or can be gathered through experiments, in order to document the dose-response relationship(s) over the range of observed doses. However, frequently this range of observation may not include sufficient data to identify a dose where the adverse effect is not observed in the human population. The second step consists of extrapolation to estimate the risk (probably of adverse effects) beyond the lower range of available observed data in order to make inferences about the critical region where the dose level begins to cause the adverse effect in the human population (USEPA, 2009).

Exposure assessment is the process of measuring or estimating the magnitude, frequency, and duration of human exposure to an agent in the environment, or estimating future exposures for an agent that has not yet been released. An exposure assessment includes some discussion of the size, nature, and types of human populations exposed to the agent, as well as discussion of the uncertainties in the above information. Exposure can be measured directly, but more commonly is estimated indirectly through consideration of measured (USEPA, 2009).

In this study, five scenarios are assumed to estimate the human exposure to OPAL and ULP. In these five scenarios, the intakes/doses of OPAL and ULP through inhalation and ingestion are calculated. In this study, the doses of the different chemicals of concern are assumed to be administered dose. The factors to be considered in determining the intake

of contaminants include considerations of life style, frequency and duration of exposure (e.g., chronic, subchronic, or acute), and the body weight of the receptor. In the majority of hazardous waste sites, long-term exposures are frequently of greatest concern.

Therefore, the calculation of an administered dose is summarized in the following generic equation:

$$I = \frac{C \times CR \times EF \times ED}{BW \times AT}$$

Equation 3.2 (LaGrega et al., 2001)

Where I = intake (mg/kg of body weight · day),

C = concentration at exposure point (e.g., mg/L in water or mg/m³ in air),

CR = contact rate (e.g., L/day or m³/day),

EF = exposure frequency (days/year),

ED = exposure duration (years),

BW = body weight (kg), and

AT = averaging time (days)

There might be some variants of this equation in order to calculate the dose of certain specific component, but this is the basic equation for calculating the administered dose.

Risk characterization is to summarize and integrate information from the proceeding steps of the risk assessment to synthesize an overall conclusion about risk (USEPA,

2009). In this study, this stage consists of calculating quantitative estimates of both the carcinogenic and non-carcinogenic risks to receptors for all five exposure scenarios considered. Carcinogenic risk may be defined as the daily intake dose multiplied by the carcinogenic slope factor. Slope factor comprises a plausible upper bound estimate of the probability of a response per unit intake of a chemical over a lifetime. It is used to evaluate the probability of cancer development due to a lifetime of exposure (SENES Consultants Limited, 2006). The computation is as follows:

$$Risk = I \times SF \quad \text{Equation 3.3}$$

Where I = daily intake of carcinogen, mg/kg-day

SF = carcinogen slope factor, kg-day/mg

Non-carcinogenic risk is normally characterized in terms of a hazard index. This index is simply the ratio of the estimated intake dose from exposure to the reference concentration (RfC). RfC comprises an estimate of the daily exposure level for a chemical for the entire population, including sensitive populations such as the elderly, children and pregnant women (SENES Consultants Limited, 2006). The hazard index is calculated as follow:

$$HI = I / RfC \quad \text{Equation 3.4}$$

Where HI = hazard index (dimensionless)

I = daily intake of non-carcinogen, mg/kg-day

RfC = reference concentration, mg/kg-day.

If the acceptable level of intake is considered to equal the reference dose, then by definition, a hazard index less than 1.0 is acceptable (LaGrega et al., 2001)

Chapter 4 Application of RBLCA to OPAL and ULP

4.1 Defining the goal and scope

The goal of this study is to estimate the environmental and human health impact of OPAL in the consumption stage, and its comparison to ULP. The complete life cycle of OPAL is supposed to include crude oil extraction, production, transportation, refining, and eventual consumption. Since OPAL and ULP undergo the same processes for extraction, the production of crude oil stage, the refining gasoline stage, and the transportation of gasoline stage, the amount of emission and wastes generated during these processes for OPAL and ULP are assumed to be the same. However, due to different specifications of OPAL and ULP, the emissions and wastes in the consumption stage are significantly different. Given the main purpose of this study, the RBLCA of OPAL and ULP in the consumption stage is only concentrated on in this study. Figure 3 shows the general system boundary of RBLCA in this study.

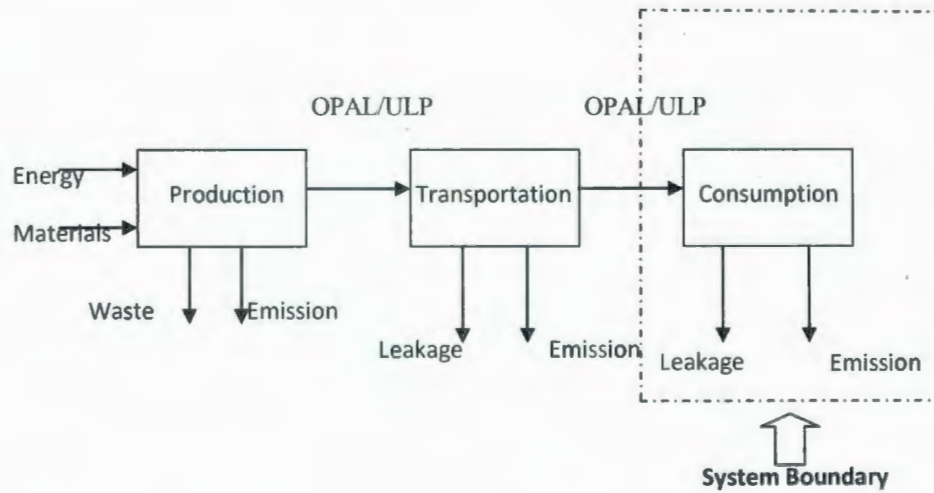


Figure 3 System boundary of RBLCA in this study

4.2 Inventory analysis

Wastes from this stage are mainly divided into two sub-stages: motor vehicle combustion emission, and motor vehicle refuelling emissions.

Motor vehicle refuelling is an important source of volatile organic compounds (VOCs) exposure which is harmful to both the environment and human health. The source of VOCs emissions associated with refuelling is the vapours contained in vehicle fuel tanks that are displaced by gasoline during operations. Additional emissions are associated with vehicle refuelling operations as the result of “breathing losses” from underground storage tanks at gasoline service stations (Watson et al., 1988). During refuelling, customers and attendants may easily be exposed to extremely high levels of VOCs like benzene, toluene,

and xylene (BTX). Several studies have been conducted all over the world to measure VOC exposure at gasoline refuelling stations (Periago & Prado, 2005; Keprasertsup et al., 2003). However, no such measurement has been done for OPAL so far.

Internal combustion engines are large contributors to air pollution, which has a damaging impact on our health and the environment and is suspected of causing global climate changes. All internal combustion engines produce emissions of VOCs, carbon monoxide (CO), Nitrogen oxides (NO_x), particulate matter (PM), carbon dioxide (CO₂), sulphur oxides (SO_x), and greenhouse gases (GHGs) (Environment Canada, 2001). Several measurements have been conducted to estimate the tail pipe emissions of engine running on OPAL.

In 2004, BP commissioned Toyota to perform testing on the tail pipe exhaust emissions of OPAL and ULP on three cars which are AVALON, HOLDEN, and FORD. Test procedure ADR 79/00 was used to measure the tail pipe emissions of cars running on OPAL and ULP. The results are shown in the Table 3.

Table 3 Test results of tail pipe emissions

Car	Hydrocarbons (HC)		Carbon monoxide (CO)		Nitric oxide (NO)	
	OPAL g/km	ULP g/km	OPAL g/km	ULP g/km	OPAL g/km	ULP g/km
AVALON	0.03	0.09	0.10	0.12	0.13	0.10
HOLDEN	0.25	0.29	0.75	0.95	0.72	0.98
FORD	0.20	0.25	0.72	0.98	0.08	0.10

In 2006, the Orbital Engineering Service (OES) conducted the testing program on fuel consumption and fuel emission City cycle and Highway for both OPAL and ULP in October 2006. The vehicle used was a 1991 Toyota Corolla fitted with a carburetted fuel system and which had registered over 180,000 kilometres on the odometer (SWB Consulting, 2007). Test procedure ADR 37/01 and AS2877 were used to measure the tail pipe emissions of cars running on OPAL and ULP in this testing. The results of the testing are shown in the Table 4. Table 5 shows the average values of the results of two tests.

Table 4 Fuel Consumption and Tail Pipe Emission City cycle and Highway ULP and OPAL Results (OES, 2006)

	TOTAL WGTD MASS (g/km)	THC	CH ₄	CO	CO ₂	NO _x	FUEL	
							g/km	l/100km
Test 1 for ULP	ADR37/01	0.689	0.00	16.95	181.1	0.191	66.18	8.84
	AS2877	0.603	0.00	16.11	131.7	0.119	50.11	6.69
Test 2 for ULP	ADR37/01	0.662	0.00	15.22	182.2	0.232	65.63	8.76
	AS2877	0.647	0.00	16.48	131.6	0.126	50.31	6.71
Test 1 for OPAL	ADR37/01	0.752	0.00	15.84	171.9	0.126	62.79	9.02
	AS2877	0.691	0.00	16.23	125.7	0.094	48.36	6.94
Test.2 for OPAL	ADR37/01	0.747	0.00	15.36	172.0	0.118	62.59	8.99
	AS2877	0.702	0.00	15.66	125.6	0.062	48.05	6.90

Table 5 Average Tests Results of Tail Pipe Emission for OPAL and ULP

TOTAL WGTD MASS (kg/km)	THC	CH ₄	CO	CO ₂	NO _x
OPAL					
ADR37/01	7.50E-04	0.00	1.560E-02	0.172	1.22E-04
AS2877	6.97E-04	0.00	1.595E-02	0.126	0.78E-04
ULP					
ADR37/01	6.76E-04	0.00	1.609E-02	0.182	2.11E-04
AS2877	6.25E-04	0.00	1.630E-02	0.132	1.23E-04

4.3 Impact assessment

The results of the inventory analysis need to be processed and interpreted in terms of the potential and actual environmental impacts and human health effects in order to complete the assessment and comparison (Khan et al., 2002). Since the testing for OPAL and ULP

by OES took into consideration more types of tail pipe emissions, their results were chosen to be used to examine the environmental and human health impacts of OPAL in the impact assessment. In addition, the testing for OPAL and ULP by OES were conducted in the same conditions, therefore, the results can be compared in order to identify which gasoline has less adverse impacts on human health and the environment.

4.3.1 Classification

The classification stage requires the identification of inventory data relevant to each specific impact category and assignment of the appropriate LCI results to each category (McDougal & White, 2001). Based on the results from the testing, ecosystem damage and human health damage are classified to be main concerns.

4.3.2 Characterization

In motor vehicle combustion emissions from inventory analysis, NO_x is contributing to the ecosystem damage by the combined effect of acidification and eutrophication. In addition, NO_x , hydrocarbons (HC), and climate change caused by CO_2 are the major contributors to human health damage. Since no detailed composition information of HCs measured by OES, it is assumed that all the HCs are volatile organic compounds.

Because of a lack of information, the following damages to human health and ecosystem quality were concentrated on:

- Respiratory effects on humans caused by total hydrocarbons (THCs)
- Respiratory effects on humans caused by NO_x
- Damage to human health caused by climate change (CO and CO₂)
- Damage to ecosystem quality caused by the combined effect of acidification and eutrophication (NO_x)

The weighted damage factor for CO was not found in the eco-indicator 99. Since carbon monoxide concentrations are short-lived in the atmosphere as a result of its eventual oxidization to carbon dioxide, the weighted damage factor of carbon monoxide was assumed to be same as carbon dioxide. Table 6 illustrates the considered emissions' fates, exposure, effects to human health or ecosystem, and damage.

Table 6 Emissions' fate, exposure and effects, and damage (Geodkoop & Spriensma, 2001)

Emission	Fate	Exposure and Effects	Damage
THC	Concentration fine dust, VOC	Respiratory effects	Damage to human health
CO	Oxidize to CO ₂ , concentration of greenhouse gas	Ozonlayer depletion (cancer + cataract)	Damage to human health
CO ₂	Concentration of greenhouse gas	Ozonlayer depletion (cancer + cataract)	Damage to human health
NO _x	Altered pH + nutrient availability	Effect on target species Respiratory effects	Damage to ecosystem and human health

According to the equation of calculating weighted damage which has been explained in the methodology chapter, the results are listed in the following tables. All the weighted damage factors are from The Eco-indicator 99 impact assessment methodology. (Geodkoop & Spriensma, 2001).

AD 37/01 testing procedure:

Table 7 Damage to human health and ecosystem by NO_x, THC, CO₂, and CO

	NO _x		THC		CO ₂		CO	
	OPAL	ULP	OPAL	ULP	OPAL	ULP	OPAL	ULP
Emission	1.22E-04	2.11E-04	7.50E-04	6.76E-04	0.172	0.182	1.560E-02	1.609E-02
Weighted damage factor for human health	2.30E+00		1.68E-02		5.45E-03		5.45E-03	
Damage to human health	2.81E-04	4.85E-04	1.26E-05	1.14E-05	9.37E-04	9.92E-04	8.50E-05	8.77E-05
Weighted damage factor for ecosystem	4.45E-01		N/A		N/A		N/A	
Damage to the ecosystem	5.43E-05	9.39E-05	N/A	N/A	N/A	N/A	N/A	N/A

AS2877 testing procedure:**Table 8 Damage to human health and ecosystem by NO_x, THC, CO₂, and CO**

	NO _x		THC		CO ₂		CO	
	OPAL	ULP	OPAL	ULP	OPAL	ULP	OPAL	ULP
Emission	0.78E-04	1.23E-04	6.97E-04	6.25E-04	0.126	0.132	1.595E-02	1.630E-02
Weighted damage factor for human health	2.30E+00		1.68E-02		5.45E-03		5.45E-03	
Damage to human health	1.79E-04	2.83E-04	1.12E-05	1.05E-05	6.87E-04	7.19E-04	6.93E-05	8.88E-05
Weighted damage factor for ecosystem	4.45E-01		N/A		N/A		N/A	
Damage to the ecosystem	3.47E-05	5.47E-05	N/A	N/A	N/A	N/A	N/A	N/A

Since the weighted damage of each emission has been calculated, the sum of them is the total damages caused by all the tail pipe emissions from the engine running on OPAL and ULP. It is clear that OPAL has less total damage to both human health and the ecosystem than ULP. Table 9 and 10 summarize the damages to human health and the ecosystem by each emission.

Table 9 Calculated weighted damages based on the results measured according to AD 37/01

	Damage to ecosystem by NO _x	Damage to human health by THC	Damage to human health by CO ₂	Damage to human health by CO	Damage to human health by NO _x	Total damage
OPAL	5.43E-05	1.26E-05	9.37E-04	8.50E-05	2.81E-04	1.37E-03
ULP	9.39E-05	1.14E-05	9.92E-04	8.77E-05	4.85E-04	1.67E-03

Table 10 Calculated weighted damages based on the results measured according to AS2877

	Damage to ecosystem by NO _x	Damage to human health by THC	Damage to human health by CO ₂	Damage to human health by CO	Damage to human health by NO _x	Total damage
OPAL	3.47E-05	1.12E-05	6.87E-04	6.93E-05	1.79E-04	0.98E-03
ULP	5.47E-05	1.05E-05	7.19E-04	8.88E-05	2.83E-04	1.16E-03

Figure 4 and Figure 5 show the total damage of OPAL and ULP based on the data measured according to AD 37/01 and AS 2877 respectively. Among various emissions, CO₂ and CO leading to climate change is a major concern to human health contributing about 72%, followed by NO_x and THC. Through comparison, it is clear that OPAL performs as the better option than ULP, because OPAL has less total damage to human health and the ecosystem than ULP.

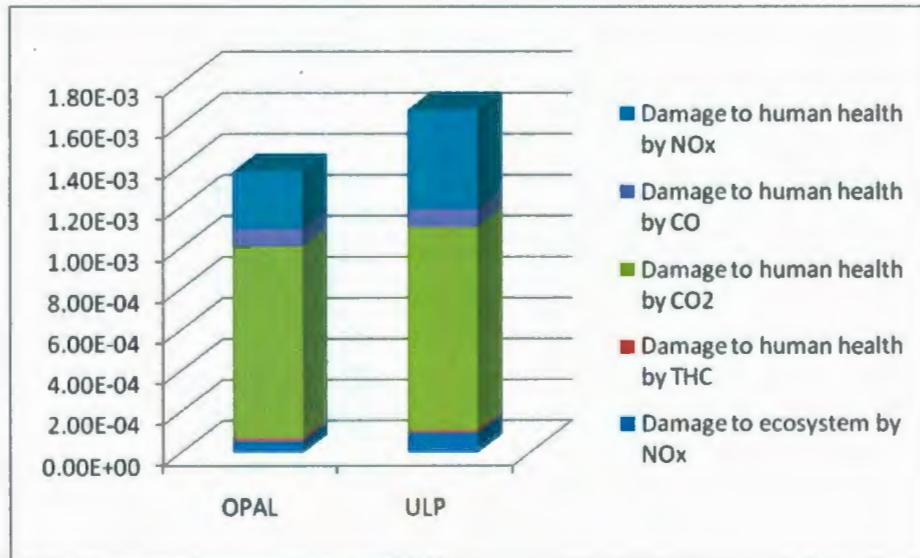


Figure 4 Final damage for OPAL and ULP based on the data measured according to AD 37/01

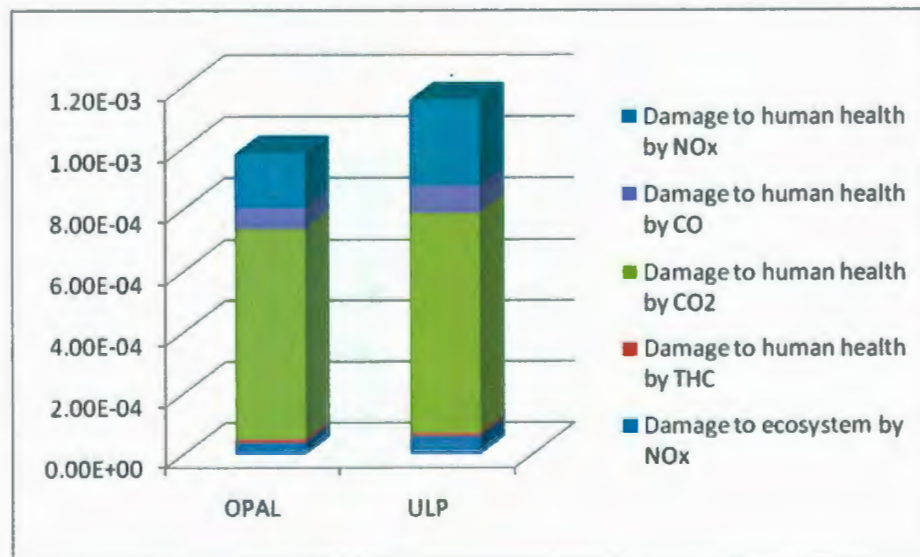


Figure 5 Final damage points for OPAL and ULP based on the data measured according to AS2877

4.3.3 Interpretation

Based on the results from impact assessment, OPAL behaves to have less damage to health by NO_x , CO_2 , and less damage to ecosystem by NO_x . However, the damage by THC for OPAL is higher than that for ULP, which means that OPAL has comparatively a higher hydrocarbon content in the combustion products than does ULP. Since the damage to human health by THC only occupies around 0.1% of the total damage in both testing, the total damage to human health and the ecosystem by OPAL is still less than that by ULP.

Since impact assessment only estimated the potential environmental and human health effects caused by OPAL and ULP during the consumption stage, the potential risks that these two types of gasoline would cause remained unknown. Therefore, it is necessary to conduct a detailed RA to estimate the potential risks.

4.4 Human health risk assessment

The purpose of introducing OPAL to remote areas is to reduce the harmful effects to human health caused by gasoline sniffing, therefore, the human health risk is the most important concern in this study. A detailed investigation has been conducted for human health risk caused by OPAL and ULP. Because of limited toxicological data, and the variability of the composition of gasoline after it is released into the environment, the human health risk assessment focuses only on four specific components: benzene, toluene,

xylene, and butane, since benzene, toluene, and xylene are the main concerns of ULP, and high content of butane would be the major concern of OPAL application in cold climates if OPAL could be used in cold climate areas, such as Labrador.

4.4.1 Hazard identification

Gasoline is considered moderately poisonous by inhalation of its vapours, by ingestion of the liquid or by skin contact (Vincoli, 1997). Generally, inhalation and skin contact are the usual routes of exposure. Ingestion usually occurs accidentally, since with normal storage and use, gasoline ingestion is an unlikely event. Because gasoline's components have different metabolic pathways, it is hard to identify the toxicokinetics of gasoline as a whole (Reese & Kimbrough, 1993).

Due to gasoline's variable composition, it is only possible to generalize about its acute toxicity. The principal target body system for gasoline toxicity is the central nervous system (CNS). The systemic effects of acute exposure are CNS depression and mimic those of ethanol inebriation. Exposure to gasoline concentrations results in flushing of the face, ataxia, staggering, vertigo, mental confusion, headaches, blurred vision, slurred speech, and difficulty swallowing. At high concentrations, coma and death may result in a few minutes without any accompanying respiratory struggle or post-mortem signs of anoxia (Reese & Kimbrough, 1993).

In addition, exposure to gasoline vapours was classified by the International Agency for Research on Cancer (IARC) in 1989 as possibly carcinogenic to humans (Group 2B). Based on many human and epidemiological studies, the onset of renal and liver cancer, acute myeloid leukemia, myeloma, nasal cancer, and pharyngeal, laryngeal, and lung cancers may have a relationship with gasoline exposure (Caprino & Togna, 1998). Besides the cancers and the effects to the CNS, gasoline may cause lesions to skin and mucous membranes, heart diseases, damage on intellectual capacity, modifications of psychomotor and visuo-motor functions, and immediate and delayed memory (Caprino & Togna, 1998).

Associated health effects caused by gasoline sniffing should be paid more attention, since most people are affected by gasoline through inhalation of evaporative vehicle emissions or emissions during fueling of automobiles. Symptoms resulting from inhalation of gasoline fumes range from lightheadedness and mild confusion to a psychosis-like state. Then, these effects are rapidly followed by nausea, vomiting, abdominal pain, agitation, and anxiety. In addition, hypomania, collapse, and coma may result. Sandmeyer illustrates that gasoline can sensitize the myocardium to the effect of endogenous or exogenous adrenergics, leading to cardiac arrhythmias (Reese & Kimbrough, 1993).

Aromatic hydrocarbons including benzene, toluene, and xylene are considered the major concern of ULP because of their comparatively higher toxicity (Periago & Prado, 2005).

Exposure to aromatic hydrocarbons is usually via inhalation, ingestion, and skin contact. The principal target organ in acute intoxication is the CNS. The systemic clinical effects after acute administration of benzene, toluene, or xylene is essentially the same and occurs in about the same dosage range via inhalation, ingestion, and injection. The symptoms, following lower inhalation or oral exposure levels, include dizziness, weakness, euphoria, headache, nausea, vomiting, tightness in the chest, and staggering. More severe exposures result in visual blurring, tremors, shallow and rapid respiration, ventricular fibrillation, paralysis, unconsciousness, and convulsions. Direct skin contact with liquids causes vasodilation, erythema, and dry and scaly dermatitis. Direct eye contact with liquid or solid aromatic hydrocarbons causes itching, lacrimation, and irritation. Toluene and benzene vapours irritate the mucous membranes of the respiratory tract. The degree of irritation for all three aromatic hydrocarbons depends on the concentration and duration of exposure (Reese & Kimbrough, 1993). Reese and Kimbrough also summarized the acutely toxic doses of aromatic hydrocarbons, which are listed in the following table. OPAL has very low levels of aromatic compounds such as benzene, toluene, and xylene (typically less than 5% volume), which are believed to be associated with the adverse effects from sniffing gasoline (BP, 2005). Therefore, aromatic hydrocarbons are not regarded as the main concern of OPAL.

Table 11 Acute toxicity of benzene, toluene, xylene (Reese & Kimbrough, 1993)

Aromatic hydrocarbon	Species	Exposure route	Dose level	Effects	Notes
Benzene	Human	Oral	128-428 mg/kg	Lethal dose range	70 kg adult
		Inhalation	61,000-64,000 mg/m ³	Potentially fatal	5-10 min
			9,600 mg/m ³	Tolerable for 30 min-1 hr	
Toluene	Human	Inhalation	376.7 mg/m ³	LOAEL; eye irritant	6-hr exposure
			380 mg/m ³	NOAEL	8-hr exposure
			750mg/m ³	Uncoordination; reaction time impaired	
		Dermal	753.4 mg/m ³	Paresthesias	8-hr exposure
		Eye	376.7-1883.4 mg/m ³	Range for irritant	
Xylene	Human	Oral	15 ml	Potential lethal dose	
		Inhalation	860 mg/m ³	Irritant-eye, nose, throat	3-5-min exposure
			>870 mg/m ³	Nausea, vomiting, dizziness, incoordination, mucous membrane irritation	
			43,000 mg/m ³	Unconscious, potentially fatal	

Notes: LD50 – lethal dose median; LC50 – lethal concentration, 50%, LOAEL – lowest observed adverse effect level; NOAEL – no observed adverse effect level.

In addition, butane is considered to present a high hazard to human health (U.S. Department of Health and Human Service & U.S. Department of Labour, 1992). Typically, up to 5 wt% butanes may be incorporated in gasoline (Lucas, 2001). OHSA illustrates that the butane content of motor fuels is 6-8 vol%. Based on the information, the content of butane in OPAL is 5~10%. The butane content in ULP has not been identified yet because of a lack of information. However, in order to be successfully used

in cold climates like Labrador, more butane will be added into OPAL to increase the RVP. According to the Woodward's requirements for butane content in Labrador, the butane content in OPAL will be increased to 13.5~15 vol%. As gasoline evaporates, butane, a volatile organic compound, is released from the gasoline, which could perhaps lead to gasoline sniffing problems. Therefore, butane is regarded as the major concern of OPAL application in cold climates.

Butane is an asphyxiant and presents a significant health hazard by displacing the oxygen in the atmosphere. Rapid evaporation of liquid from a cylinder may cause frostbite. Both liquified and gaseous butane pose a serious fire hazard when accidentally released (MESA, 1999). The National Fire Protection Association has assigned a flammability rating of 4 (extreme fire hazard) to butane. The flash point of liquefied butane is -60°C , and autoignition temperature of butane is 430°C (OSHA, 1992). Exposure to butane can occur through inhalation or eye and skin contact (OSHA, 1992). High concentrations of this gas can cause an oxygen-deficient environment. Individuals breathing such an atmosphere may experience symptoms which include headaches, ringing in ears, dizziness, drowsiness, unconsciousness, nausea, vomiting, and depression of all the senses. Under some circumstances of overexposure, death may occur. Contact with liquid or rapidly expanding gases (which released under high pressure) may cause frostbite. Symptoms of frostbite include change in skin colour to white or grayish-yellow. The pain after such contact can quickly subside. However, butane is not found on the following

lists: FEDERAL OSHA Z LIST, NTP, IARC, CAL/OSHA, and therefore is neither considered to be nor suspected to be a cancer-causing agent by these agencies (MESA, 1999).

Since the compositions of OPAL and ULP are different, the adverse impacts to human health by them would be different. Therefore, it is hard to generalize whether OPAL has less adverse impacts on human health than ULP.

4.4.2 Dose-response assessment

For the purposes of quantifying human health risks, chemicals are characterized as carcinogens and non-carcinogens. Dose-response relationships for carcinogens are conventionally reported as incidence of lifetime cancer versus dose. The slope, known as the slope factor, represents the carcinogenic potency for the chemical. Unlike carcinogens, non-carcinogens exhibit a threshold effects. Namely, below a specific dose, they fail to induce any adverse health effect in exposed populations. This threshold is defined as the reference concentration (RfC), which is the estimated daily intake that is not believed to be associated with adverse health effects (LaGreg et al., 2001).

Considerable measurements have been conducted to study the dose-response relationship of benzene, toluene, and xylene. Table 12 shows the slope factor (SF) for benzene, and Table 13 shows the reference concentrations for toluene and xylene.

Table 12 Toxicity values for evaluation of carcinogenic effects (Hoddinott, 1992)

Chemical	Cancer Group	Inhalation SF (kg-day/mg)	Oral SF (kg-day/mg)
benzene	A	2.9E-02	2.9E-02

Table 13 Toxicity values for evaluation of non-carcinogenic effects (Hoddinott, 1992)

Chemical	Inhalation RfC (mg/kg-day)	Oral RfD (mg/kg-day)
toluene	6E-01	2E-01
xylene	9E-02	2E+00

Few studies about butane dose-response relationships were found. However, several studies were conducted to measure the exposure limits of butane. The permissible exposure limit (PEL) of the current Occupational Safety and Health Administration (OSHA) for butane is 800 ppm (1,900 mg/m³) as an 8-hr time-weighted average (TWA). The National Institute for Occupational Safety and Health (NIOSH), and the American Conference of Governmental Industrial Hygienists (ACGIH) established 800 ppm (1,900 mg/m³) as a TWA for a normal 8-hr workday and a 40-hr workweek. Therefore, the no observed adverse effect level (NOAEL) of butane for an attendant every day is 1,900 mg/m³. The intake equation can be applied to express this concentration in mg/(kg-day).

$$I = \frac{1,900 \times 0.46 \times 2000 \times 5}{70 \times 10950} = 11.40 \text{ mg / kg} \cdot \text{day} \quad \text{Equation 4.1}$$

Therefore, 11.40 mg/kg-day can be regarded as the RfC of butane for a gasoline service station attendant. No information of NOAEL of butane for a 24-hr exposure was found. Therefore, a 11.40 mg/kg-day is also used as the RfC for calculating the risk of an individual residing 100 m downwind of a nearby gasoline service station who inhales gasoline vapour emission associated with service station operations.

4.4.3 Exposure assessment

Gasoline exists in the environment in four states: as a free-moving liquid, absorbed into soil, in groundwater, and as an aerosol or vapour (Periago & Prado, 2005). The presence of benzene, toluene, xylene (BTX), and butane are considered as the main concern of ULP and OPAL to human health because of their high content and high hazardous level. Therefore, the components of concern selected for this assessment are benzene, toluene, xylene, and butane. Since all these four components are volatile organic compounds, gasoline vapour emissions and motor vehicle exhausts are regarded as significant sources of exposures (Lee et al., 2002). In addition, since benzene, toluene, and xylene have high water solubilities, they may exist in the water soluble fraction of gasoline (NESCAUM, 1989).

It is well known that motor vehicle exhaust is a significant source of air pollution, and unburned hydrocarbons are considered as one of the most widely reported pollutants in vehicular exhaust (Brugge et al., 2007). The Orbital Engineering Service (OES) conducted the testing program on fuel emission (City cycle and Highway) for both OPAL and ULP. The results show that OPAL has slightly more total hydrocarbons in the exhaust emissions than ULP. However, since the composition of total hydrocarbons of OPAL and ULP released in the exhaust emissions are unknown, it is hard to identify which gasoline is more harmful to human health.

Gasoline service stations are also the important sources of gasoline vapour emissions. Sources of gasoline vapours at service stations include losses from underground tanks, displacement vapour losses from filler pipes during refuelling, fuel spillage and evaporative and tailpipe emissions from motor vehicles (NESCAUM, 1989). Although there is no study for OPAL and ULP, several studies have been conducted to measure the concentration of gasoline vapour emission at the refuelling sites, specifically the concentrations of aromatics such as benzene, toluene, and xylene. However, few studies were found that measured the butane concentration at the refuelling sites. Periago and Prado conducted a study to measure the time-weighted average concentrations of aromatic compounds in occupationally exposed workers of refuelling stations in July 2003 in Spain. The general environmental and personal sampling conditions on refuelling stations are listed in the following table.

Table 14 Environmental and personal sampling conditions on refuelling stations (Periago & Prado, 2005)

Period	No. Of workers	Sampling time (min)	Temperature (°C)	Gasoline dispensed (l)	% of unleaded gasoline dispensed
2003	19	300-450	35-36	303-4250	81

The results from this study are showed in the Table 15.

Table 15 Time-weighted average concentrations of aromatic compounds in occupationally exposed workers of refuelling station (Periago & Prado, 2005)

Period	No. Of samplers	Compound	Mean (mg/m ³)	SD (mg/m ³)	Range
2003	19	Benzene	0.163	0.132	0.35-0.564
2003	19	Toluene	0.753	0.551	0.172-0.2142
2003	19	Xylene	0.316	0.084	0.125-0.871

During the summer of 2002, Keprasertsup and his colleagues measured the BTX in ambient air at gas stations in Bangkok and the surrounding area. Since the volumes of gasoline sold affect the concentration in ambient air significantly, the measurements are divided into two parts: the concentration of BTX when the gas station experienced high sales (474-1,100 L/h) and the concentration of BTX when gas station had low sales (92-393 L/h) The measured concentrations of benzene, toluene, and xylene at two sample gas stations are listed in the following table.

Table 16 Concentrations of VOCs ($\mu\text{g}/\text{m}^3$) at the sample gas station (Keprasertsup et al., 2003)

Period	No. Of samples	Compound	Mean (mg/m ³)		SD (mg/m ³)	Range
2002	18	Benzene	High sale	0.175	0.137	0.048-0.386
			Low sale	0.147	0.009	0.05-0.028
2002	18	Toluene	High sale	0.460	0.333	0.148-0.975
			Low sale	0.088	0.032	0.044-0.131
2002	18	Xylene	High sale	0.212	0.139	0.017-0.383
			Low sale	0.064	0.022	0.036-0.095
2002	18	Benzene	High sale	0.025	0.017	0.007-0.047
			Low sale	0.006	0.005	0.001-0.013
2002	18	Toluene	High sale	0.070	0.042	0.037-0.129
			Low sale	0.044	0.041	0.021-0.128
2002	18	Xylene	High sale	0.033	0.019	0.012-0.066
			Low sale	0.023	0.017	0.005-0.050

When gasoline enters groundwater, such as from a leaking storage tank, it tends to remain more like the original mixture. Since gasoline is confined underground, there will be only limited evaporation of the more volatile components. However, the more water-soluble compounds will dissolve in the groundwater and may become widely distributed in the subsurface water (Health Canada, 1986). Because some organic constituents of gasoline were detected in water in Canada, Health Canada conducted studies to measure the concentration of these organic components in Canadian drinking water supplies. Since benzene, toluene, and xylene are highly water soluble compared to butane, only BTX are considered to be concerns. Based on the results, mean concentrations of benzene ranged from 0.001~0.003 mg/L, and a maximum value of 0.048 mg/L. In a study of Ontario

drinking water, toluene and xylene were found at concentrations ranging from the detection limit of 15 ng/L to 500 ng/L (Environment Canada, 1986). Concentrations of toluene in Canadian drinking water supplies averaged 2.0 µg/L and ranged up to 27 µg/L at 30 water treatment plants across Canada in a survey conducted in 1979 (Environment Canada, 1992). The mean concentrations of xylenes in Canadian drinking water supplies, at 30 water treatment plants sampled across Canada in 1979, were less than 1 µg/L. In more recent surveys of water supply systems conducted in Ontario in 1987 and in the Atlantic provinces between 1985 and 1987, concentrations of xylenes were generally less than the detection limit of 0.5 µg/L (Environment Canada, 1992). Since these measurements were conducted around 1986 and commercial gasoline at that time contained 14 to 33% aromatic compounds which is similar to ULP's aromatic contents, the results of measurements will be closer to that of ULP.

In this assessment, five exposure scenarios are selected for analysis in details:

- A full-time service station attendant inhaling gasoline vapours;
- An individual residing downwind of a nearby gasoline service station inhaling gasoline vapour emission associated with service station operations;
- An individual resident ingesting gasoline contaminated water;
- Scenario #1 conducted in cold climates; and

- Scenario #2 conducted in cold climates.

Scenario #1

In scenario #1, the daily intakes of OPAL/ULP that a full-time service station attendant inhales are estimated.

Since no experiment has been conducted, some basic assumptions have to be made because of data gap, environmental fate complexities, and the need to generalize the receptors characteristics. Based on Keprasertsup and his colleagues' experiments, an average 15 m³ volume of gasoline is assumed to be sold at a gasoline service station in warm climates every day, and 0.1% of the 15 m³ gasoline is lost through spill, evaporation, or other ways. The service station is assumed to be a 1000 m³ room. The ambient temperature is 25°C at 1 atm. According to OPAL's specifications, it contains 1 vol% benzene, 5 vol% toluene and xyxylene, and 5-10 vol% butane. Therefore, the OPAL sold in the service station in the scenario #1 is assumed to contain 1 vol% benzene, 4 vol% toluene, 1 vol% xylene, and 10 vol% butane. Similarly, ULP contains 1 vol% benzene, and 25 vol% toluene and xylene. Therefore, the ULP sold in the service station in the scenario #1 is assumed to contain 1 vol% benzene, 20 vol% toluene, 5 vol% xylene. However, the butane content in ULP remains unknown. Since SWB Consulting

illustrated that ULP has similar specifications to OPAL, in order to simplify the study, the butane content in ULP is also assumed to be 10 vol% (SWB Consulting, 2007).

The receptor used in this scenario to characterize potential risks associated with the refuelling operations in the service station is assumed to be exposed for five years, 8 hours each day of the year. An exposure duration of 5 years was selected based upon the estimated duration which an attendant works in a service station. The following table shows the summary of the receptor characteristics. These values can vary greatly, depending on the assumed exposure conditions.

Table 17 Summary of receptor characteristics (Adult)

Parameter	Units	Value	Reference
Contact Rate (CR)	m ³ /h	0.46	LaGrega et al. 2001 as recommended by USEPA, 1993
Exposure Frequency (EF)	h/yr	2000	Assumption
Exposure Duration	yr	5	Assumption
Body Weight	kg	70	Richardson 1997 as recommended by Health Canada, 2004
Average Time (carcinogen)	d	25550	Assumption
Average Time (non-carcinogen)	d	10950	Assumption

According to these assumptions, the volumes of liquid benzene, liquid toluene, liquid xylene, and liquid butane lost every day at the gasoline service station are listed in the following table.

Table 18 Volume of liquid benzene, toluene, xylene, and butane in OPAL/ULP lost every day

	ULP(10^{-3} m ³ /day)	OPAL(10^{-3} m ³ /day)
Benzene	0.150	0.150
Toluene	3.000	0.600
Xylene	0.750	0.150
Butane	1.500	1.500

Mehlman illustrated the vapour phase to liquid phase (V/L) ratio which assisted to calculate the volume of refuelling vapours of each component. Table 19 shows the refuelling vapour/dispensed liquid ratios for hydrocarbon components in one type of gasoline, the composition of which is similar to ULP.

Table 19 Refueling Gasoline Vapours/Dispensed Liquid Gasoline ratios for hydrocarbon components (Mehlman, 1990)

Compound	Refueling Vapour/Dispersed Liquid ratios (S/W)
butane	7.6/6.2
benzene	0.34/0.21
toluene	0.10/0.05
xylene	0.04/0.007

Notes: Based on average summer and winter blends. S/W = Summer/Winter

Assume both ULP and OPAL are summer blend gasoline. The volume of daily released vapour of ULP is calculated and demonstrated in Table 20.

Table 20 Volume of gaseous benzene, toluene, xylene, and butane lost in the service station every day

	ULP(10^{-3} m ³ /day)	OPAL(10^{-3} m ³ /day)
Benzene	0.045	0.045
Toluene	0.300	0.060
Xylene	0.030	0.006
Butane	11.400	11.400

Since the specific gravity of each component is known, the mass amount of gaseous components can be calculated. Based on the literature review, the density of air is 1.184 kg/m³.

Table 21 Density of gaseous benzene, toluene, xylene, and butane (Environment Canada, 1992)

	benzene	toluene	xylene	butane
Specific gravity	2.7	3.18	3.66	2.01
Density	3.197 kg/m ³	3.765 kg/m ³	4.333 kg/m ³	2.380 kg/m ³

Mass amount of gaseous benzene, toluene, xylene, and butane lost from gasoline service stations each day are listed in the Table 22.

Table 22 Mass amount of gaseous benzene, toluene, xylene, and butane lost every day

	ULP(10^{-3} kg/day)	OPAL(10^{-3} kg/day)
Benzene	0.144	0.144
Toluene	1.128	0.226
Xylene	0.130	0.026
Butane	27.132	27.132

Based on the assumptions, the gasoline service station can be regarded as a 1000 m^3 space, therefore the concentration of each gaseous component in the station can be calculated.

Table 23 Mean concentrations of gaseous components at the gasoline service station every day

	ULP(mg/m^3)	OPAL(mg/m^3)
Benzene	0.144	0.144
Toluene	1.128	0.226
Xylene	0.130	0.026
Butane	27.132	27.132

These two sets of data are similar to those in the Keprasertsup and his colleagues' study, which illustrates that the assumptions are appropriate.

The final step is to estimate the amount of each component to which attendants are potentially exposed at the gasoline service station. According to the calculation equation

2 explained in chapter 3, the intake of each component for an attendant at gasoline service station every day can be calculated.

Table 24 Daily intake of each component for an attendant at gasoline service station

	Intake (Benzene) (mg/kg · day)	Intake (Toluene) (mg/kg · day)	Intake (Xylene) (mg/kg · day)	Intake (Butane) (mg/kg · day)
ULP	3.70E-04	6.77E-03	7.80E-04	0.163
OPAL	3.70E-04	1.35E-03	1.56E-04	0.163

Scenario #2

In scenario #2, the intakes of OPAL/ULP for a nearby resident who inhales gasoline vapour emission associated with service station operations are calculated.

For no experiment has been conducted, basic assumptions are established. Firstly, the risk for a resident living 100 m away from the service station in the scenario #1 is assumed. Gasoline vapour is assumed to be continuously released and only ground level centerline concentration of each component is considered. In order to obtain the worst case, the stability class is classified as F which is moderately to strongly stable condition, and the surface wind speed is 2 m/s. The height of releasing source is 0 m. The resident receptor characteristics are summarized in the following table.

Table 25 Summary of receptor characteristics (Adult)

Parameter	Units	Value	Reference
Contact Rate (CR)	m ³ /h	0.46	LaGrega et al. 2001 as recommended by USEPA, 1993
Exposure Frequency (EF)	d/yr	365	Assumption
Exposure Duration	Yr	30	Assumption
Body Weight	Kg	70	Richardson 1997 as recommended by Health Canada, 2004
Average Time (carcinogen)	D	25550	Assumption
Average Time (non-carcinogen)	D	10950	Assumption

Based on the assumptions, dispersion coefficient can be calculated according to the following equations:

$$\sigma_y = 0.11X(1 + 0.0004X)^{-0.5} = 0.11 \times 100(1 + 0.0004 \times 100)^{-0.5} = 11m \quad \text{Equation 4.2}$$

$$\sigma_z = 0.08X(1 + 0.0015X)^{-0.5} = 0.08 \times 100(1 + 0.0015 \times 100)^{-0.5} = 7m \quad \text{Equation 4.3}$$

The concentration of each component 100 m away can be calculated through the following equation:

$$C(x,0,0) = \frac{Q}{\pi\sigma_z\sigma_y U} \quad \text{Equation 4.4}$$

Since the average amount of each component released every day in the gasoline service station has been calculated in scenario #1, the concentration of gasoline vapours 100 m away from the gasoline service station can be known. The results are listed in Table 26.

Table 26 Concentrations of gaseous components 100 m away from the gasoline service station per day

	ULP(mg/m ³)	OPAL(mg/m ³)
Benzene	3.44E-12	3.44E-12
Toluene	2.70E-11	0.54E-11
Xylene	3.11E-12	0.62E-12
Butane	6.49E-10	6.49E-10

According to the intake equation, the intake of each component for the residents who live 100 m away from the gasoline service station can be calculated.

Table 27 Daily intake of each component for an individual living 100m away from the gasoline service station

	Intake (Benzene) (mg/kg · day)	Intake (Toluene) (mg/kg · day)	Intake (Xylene) (mg/kg · day)	Intake (Butane) (mg/kg · day)
ULP	2.33E-13	4.26E-12	4.90E-13	10.24E-11
OPAL	2.33E-13	0.85E-12	0.98E-13	10.24E-11

Scenario #3

In scenario 3, the intakes of OPAL/ULP for an individual ingesting gasoline contaminated water are evaluated.

The water solubility of benzene, toluene, xylene, and butane are listed in the following table. Since butane is much less water soluble than the other three component, the adverse effects caused by butane can be omitted in this scenario.

Table 28 Water solubility of benzene, toluene, xylene, and butane (Health Canada, 1993)

Component	Water Solubility (mg/L) at 25°C
Benzene	820 ~ 2167
Toluene	535
Xylene	160 ~ 220
Butane	0.61

For no experiment has been conducted, basic assumptions are established. According to the previous assumption, ULP contains 1 vol% benzene, 20 vol% toluene, 5 vol% xylene, and 10 vol% butane; OPAL contains 1 vol% benzene, 4 vol% toluene, 1 vol% xylene, and 10 vol% butane. When ULP enters the drinking water supplies through spills or leaking, the mean concentration of benzene is assumed to be 3 mg/m^3 , the mean concentration of toluene is assumed to be 2 mg/m^3 , and the mean concentration of xylene exposure is 0.5 mg/m^3 based on the studies conducted by Environment Canada in 1986. Similarly, according to the volume percentage of each component in OPAL and ULP, the mean benzene concentration is assumed to be 3 mg/m^3 , the mean concentration of toluene is 0.4 mg/m^3 , and the mean concentration of xylene is 0.1 mg/m^3 . The resident receptor characteristics are summarized in the following table.

Table 29 Summary of receptor characteristics (Adult)

Parameter	Units	Value	Reference
Contact Rate (CR)	m ³ /day	0.002	LaGrega et al. 2001 as recommended by USEPA, 1993
Exposure Frequency (EF)	d/yr	365	Assumption
Exposure Duration	yr	30	Assumption
Body Weight	kg	70	Richardson 1997 as recommended by Health Canada, 2004
Average Time (carcinogen)	d	25550	Assumption
Average Time (non-carcinogen)	d	10950	Assumption

According to the assumptions and the intake equation, the intake of each component for an individual through daily ingestion of drinking water every day can be calculated.

Table 30 Daily intake of each component for an individual through ingesting drinking water

	Intake (Benzene) (mg/kg · day)	Intake (Toluene) (mg/kg · day)	Intake (Xylene) (mg/kg · day)
ULP	3.67E-05	5.71E-05	0.61E-05
OPAL	3.67E-05	1.14E-05	0.12E-05

Scenario #4

OPAL is designed for warm climates, so it may not be applicable in cold climate areas. For instance, it is possible for OPAL to experience cold start problem because of their low volatility if they are used in cold climates. However, if OPAL could be used in cold climates, the impacts on human health would be estimated in the following scenarios.

Therefore, the daily intakes of OPAL/ULP for an attendant through inhalation in service station in cold climates are estimated in this scenario.

First of all, some basic assumptions are needed to be established. The content of benzene, toluene, and xylene in both OPAL and ULP remain the same. Since gasoline needs higher butane content in cold climates to increase the vapour pressure to prevent the cold-start problem, the butane content in OPAL may increase in this scenario. The requirements for butane content in gasoline in different locations are not the same. Through literature review, Woodward's, the only supplier of gasoline in Labrador, requires that the minimum butane content in gasoline used in Labrador is 13.5 vol% and the maximum is 15 vol%. Therefore, it is assumed that butane content in OPAL is 15% and the butane content in ULP is 13.5% in this scenario. Other parameters are same as the ones in the scenario #1.

According to the calculation procedure in scenario #1, the daily intake of a full-time service station attendant through inhaling gasoline vapours can be obtained. Table 31 shows the results.

Table 31 Daily intake of OPAL/ULP for a full-time service station attendant through inhalation

	Intake (Benzene) (mg/kg · day)	Intake (Toluene) (mg/kg · day)	Intake (Xylene) (mg/kg · day)	Intake (Butane) (mg/kg · day)
ULP	3.70E-04	6.77E-03	7.80E-04	0.220
OPAL	3.70E-04	1.35E-03	1.56E-04	0.245

Scenario #5

Similarly, the daily intakes of OPAL/ULP for a resident living close to the service station through inhalation in the cold climates is estimated in this scenario in the case that OPAL is assumed to be applicable in cold climates.

The basic assumptions established are almost the same as those assumed in the scenario #4. The content of benzene, toluene, and xylene in both OPAL and ULP remain the same. But the butane content in OPAL increases to 15% and the butane content in ULP increases to 13.5%. Other parameters are same as the ones in the scenario #2.

According to the calculation procedure in scenario #2, the daily intake of an individual resident downwind of the nearby gasoline service station inhaling gasoline vapour emission associated with service station operations can be obtained. Table 32 shows the results.

Table 32 Daily intake of OPAL/ULP for a resident living 100 m away from the gasoline service station

	Intake (Benzene) (mg/kg · day)	Intake (Toluene) (mg/kg · day)	Intake (Xylene) (mg/kg · day)	Intake (Butane) (mg/kg · day)
ULP	2.33E-13	4.26E-12	4.90E-13	13.82E-11
OPAL	2.33E-13	0.85E-12	0.98E-13	15.36E-11

4.4.4 Risk characterization

The final stage of human health risk assessment is to estimate risks. It consists of calculating quantitative estimates of both the carcinogenic (benzene) and non-carcinogenic (toluene, xylene, and butane) risks to receptors for all three exposure scenarios considered. According to the equations above, risks in five scenarios can be calculated. The results are listed in the following tables. Based on the results, it is clearly shown that OPAL has less risk than ULP in all three scenarios, which means OPAL is safer for human health than ULP. Table 33 shows the risks of daily intake of carcinogen (benzene) in all five scenarios.

Table 33 Risks of daily intake of carcinogen (benzene)

	Risk				
	Scenario #1	Scenario #2	Scenario #3	Scenario #4	Scenario #5
ULP	1.07E-05	6.76E-15	1.06E-06	1.07E-05	6.76E-15
OPAL	1.07E-05	6.76E-15	1.06E-06	1.07E-05	6.76E-15

Table 34 shows the risks of daily intake of non-carcinogens (toluene, xylene, and butane) in all five scenarios.

Table 34 Risks of daily intake of non-carcinogens

		Risk			
		Toluene	Xylene	Butane	Total
Scenario #1	ULP	0.011	0.004	0.014	0.029
	OPAL	0.002	0.001	0.014	0.017
Scenario #2	ULP	7.10E-12	2.45E-12	8.98E-12	1.85E-11
	OPAL	1.42E-12	0.61E-12	8.98E-12	1.10E-11
Scenario #3	ULP	2.86E-04	0.31E-05	N/A	2.89E-04
	OPAL	0.57E-04	0.06E-05	N/A	0.58E-04
Scenario #4	ULP	0.011	0.004	0.019	0.034
	OPAL	0.002	0.001	0.021	0.024
Scenario #5	ULP	7.10E-12	2.45E-12	1.21E-11	2.17E-11
	OPAL	1.42E-12	0.61E-12	1.35E-11	1.55E-11

4.5 Uncertainty analysis

Many areas of uncertainty attend a risk assessment, for assumptions have to be made throughout the assessment either due to data gaps, environmental fate complexities or in the generalization of receptor characteristics. In order to have confidence in the results, an accounting of the uncertainty must be completed. In recognition of these uncertainties, cautious assumptions are used throughout the assessment to ensure that the potential for an adverse effect would not be underestimated. Several of the major assumptions are

outlined below. These assumptions should be validated to reduce the uncertainty and increase the confidence in the conclusions that no measurable adverse health effects would be expected from ULP or OPAL (SENES Consultants Limited, 2006).

Typical gasoline contains more than 300 individual hydrocarbons consisting primarily of paraffins, cycloparaffins, olefins, and aromatics (Roberts et al., 2001). In this assessment, only benzene, toluene, xylene, and butane have been selected as the assessed chemicals. Based on the information from the literature review, compared to other chemicals, the group of aromatic components constituted by benzene, toluene, and xylene are considered the main concern of ULP to human health. OPAL has a comparatively lower content of aromatics, but in order to be successfully applied in cold climate areas like Labrador the butane content of OPAL needs to be increased. However, butane is considered to present a dangerous hazard to human health. Therefore, benzene, toluene, xylene, and butane have been selected as the representative chemicals in this assessment.

The volume percentage of each component in the assessment has been assumed based on the literature review and the information provided by BP Australia. Among them, butane content in OPAL plays a significant role in the risk assessment. Butane content in OPAL is assumed to be 10 vol% in order to maximize the risks in scenario #1 and #2. According to the Woodward's requirement of butane content in gasoline in Labrador where the

climates is very cold, 15 vol% of butane in OPAL has been assumed in the cold climates scenarios so that higher exposure concentrations can be obtained.

The predicted volume of gasoline sold every day was based on the volume of gasoline sold in the high gasoline sale stations in Bangkok in Keprasertsup and his colleagues' studies. In practice, if OPAL is introduced to remote areas, much less gasoline will be sold compared to gasoline sales in Bangkok. Therefore, the potential impacts of emission and release from OPAL will be much lower than the predicted concentrations in this assessment.

In the scenario of calculating the intakes of gasoline vapour for a nearby resident through inhaling gasoline vapour emission associated with service station operations, the most stable dispersion condition were selected so that a larger exposure concentration can be obtained.

In the case of calculating the risk to human health through ingesting gasoline contaminated drinking water, the data from the measurements conducted in 1986 were used. The aromatic content including benzene, toluene, and xylene of gasoline is higher than the gasoline commonly used now. Therefore, the actual impacts of ingesting

gasoline contaminated drinking water will be much lower than the calculated concentrations in this assessment.

The receptors and their characteristics are selected in order to over-estimate potential exposures. For example, it was assumed that an adult residential receptor was assumed to live at their house 24 hours a day, 365 days a year for 30 years with no time away from the site for vacation, working off-site, or for other such reasons. This scenario is unlikely to occur and this results in a larger exposure concentration (SENES Consultants Limited, 2006). In addition, it is also assumed that a gasoline station attendant will keep working in the same place for 5 years, which is very unlikely in real life. So this scenario also results in a larger exposure concentration.

Physical-chemical properties of OPAL are obtained from the information provided by BP Limited Australia. The physical-chemical properties of ULP are summarized based on literature review. The toxicity information of four representative chemicals, benzene, toluene, xylene, and butane, are also from the literature review. However, some assumptions were made in absence of available data from the sources. For example, except benzene, the volume percentage of toluene, xylene, and butane in ULP and OPAL were assumed based on literature review.

Using a single value for toxicity is another source of uncertainties. The slope factor for benzene and the reference concentration for toluene, xylene and are chosen based on considerable literature review. The reference concentration of butane for an attendant working 8 hour a day was calculated based on the OSHA, NIOSH, and AULPIH's studies. However, because of a lack of information, the reference concentration for calculating the risk of an individual residing 100 m downwind of a nearby gasoline service station inhaling gasoline vapour emission associated with service station operations is assumed to be the same as that for the gasoline station attendant.

In summary, cautious assumptions were used in order to over-predict the exposure to emission and release from ULP and OPAL. Since the main purpose of this study is to compare the human health risk between ULP and OPAL, the uncertainties caused by assumptions will not change the overall conclusion which indicates that OPAL has less risk to human health than ULP.

Chapter 5 Discussion

Both OPAL and ULP were studied and compared in the Chapter 4. The potential environmental impacts of OPAL and ULP in the IA represented in Figure 4, 5 have been evaluated using life cycle impact assessment. Total impacts for OPAL are significantly lower than those of ULP. OPAL is found to reduce total emissions by 18% according to AD 37/02 standard; and by 16% according to AS 2877 standard compared to ULP.

Eutrophication and acidification have been identified as the only concerns to the ecosystem based on the results. The eutrophication and acidification profiles of OPAL and ULP are dominated by the emissions of NO_x from each transportation system. For OPAL, the damages to ecosystem quality caused by the combined effects of acidification and eutrophication because of the release of NO_x occupy 4% of the total damage according to AD 37/01 and AS 2877.

Among all the emissions studied in IA, CO_2 , CO, and nitrous oxide (N_2O) are considered the main greenhouse gases (GHG) in the Earth's atmosphere. GHG greatly affect the temperature of the Earth leading to Global Warming Potential (GWP) which is also a damage to ecosystem (Environmental Canada, 2009). However, there is no indicator for the damage to ecosystem quality caused by GHGs in the Eco-indicator 99 methodology, which could lead to underestimate the total damage to the ecosystem caused by OPAL. In

addition, since the composition of the THC released remains unknown, the damage to ecosystem quality caused by ecotoxic emissions is omitted. This also leads to the underestimation of the damage to ecosystem caused by OPAL.

In the analysis of the damages to human health by various emissions, the damage to human health caused by climate change because of the release of CO₂ and CO is considered the primary concern for both OPAL and ULP. For OPAL, the damages to ecosystem quality caused by climate change occupy 68% and 70% of the total damage according to AD 37/01 and AS 2877 respectively.

Hydrocarbons are commonly considered very harmful to human health, while for OPAL, the damages to human health caused by THC only occupy 1% of the total damages according to AD 37/01 and AS 2877 respectively. The reasons for this are summarized:

- i. Since the composition of hydrocarbons released is unknown, all types of hydrocarbons are assumed to be VOCs;
- ii. The amount of THC in the tail pipe emissions is significant less than the other exhaust emissions.

The fact that all types of hydrocarbons are assumed to be VOCs leads to omit to estimate the carcinogenic effects on humans and underestimate the respiratory effects on humans caused by organic substances. However, since the main purpose of the impact assessment

is to compare the damages to the environment and human health in the consumption stage caused by OPAL and ULP, these limitations can be neglected.

Through impact assessment, it is clear that OPAL has less adverse impacts on the environment and human health compared to ULP. However, the risk to human health caused by OPAL remains unknown. Since the reason of introducing OPAL is to minimize the gasoline sniffing problem in order to reduce the risk of gasoline sniffing on human health in remote areas, OPAL might also not be feasible if it would cause high risk to human health. Therefore, human health risk assessment has also been conducted. Because of a lack of information, only five scenarios were considered in this study. In Scenario #1, the occupational exposure risk in service stations by inhalation OPAL, and its comparison to ULP, was estimated. Current occupational exposure limit values corresponding to benzene, toluene, xylene, and butane set by several institutions are shown in Table 43. According to the corresponding equation and parameters assumed in scenario #1, the occupational exposure limit intakes for benzene, toluene, xylene, and butane can be calculated. The results are shown in Table 35.

Table 35 Exposure limit values for benzene, toluene, xylene, and butane (Periago & Prado, 2005)

	TLV-TWA	PEL	REL
Benzene			
Ppm	0.5	1	0.1
mg/m ³	1.6	3.25	0.325
Toluene			
Ppm	50	200	100
mg/m ³	191	764	382
Xylene			
Ppm	100	100	100
mg/m ³	442	442	442
Butane			
Ppm	800	800	800
mg/m ³	1,900	1,900	1,900

Table 36 Occupational exposure limit intakes for benzene, toluene, xylene, and butane

	Limit intake (TLV-TWA) (mg/kg · day)	Limit intake (PEL) (mg/kg · day)	Limit intake (REL) (mg/kg · day)
Benzene	4.12E-03	8.23E-03	0.82E-03
Toluene	0.87	4.58	2.29
Xylene	2.65	2.65	2.65
Butane	11.40	11.40	11.40

For OPAL, based on the results from Table 24, the exposure levels of benzene is much lower than the above mentioned limit values. This is also the case for toluene, xylene, and butane. In addition, through comparing the limits to the exposure levels of each component for a full-time service station attendant in cold climates, it is clear that the exposure concentrations of benzene, toluene, xylene, and butane are also under the limits.

Therefore, the occupational exposure risk in service stations by inhalation of OPAL is practically negligible.

The daily intake of benzene for an attendant in gasoline station by inhalation of OPAL is same as that of ULP. The daily occupational exposure levels of toluene and xylene by inhaling OPAL is much less than that of ULP, but the daily intake of butane by inhaling OPAL is much higher than that of ULP. In sum, the total occupational exposure risk in service stations by inhalation of OPAL is less than ULP.

In Scenario #2, the exposure risk for an individual living 100 m away from the service station by inhalation OPAL, and its comparison to ULP, was evaluated. There is no specific exposure limits for residing benzene, toluene, xylene, and butane exposures. So it is hard to estimate whether the daily intakes of benzene, toluene, xylene, and butane for an individual by inhaling OPAL exceed the NOAEL of these components in this scenario. However, the exposure concentration of these components for an individual residing 100 m away from the service station is closely associated with the concentration of the components in service station. Since the occupational exposure levels of benzene, toluene, xylene, and butane are very much lower than the exposure limit values, and the occupational exposure risk in service stations by inhalation of OPAL can be considered practically negligible, it is possible that the total exposure risk for an individual residing 100 m away from the service station by inhaling OPAL is also practically negligible. This

is also the case for those in cold climates. Based on the results from the risk characterization phase, OPAL has obviously less risks than ULP in this scenario, which means OPAL behaves as a safer option compared to ULP to human health.

In scenario #3, the exposure risk for an individual by ingestion of OPAL in the drinking water, and its comparison to ULP, was estimated. USEPA regulates benzene, toluene, and xylene in drinking water to protect public health. Enforceable regulations have been set for these three components, called maximum contaminant level (MCL) which is the highest level of a contaminant that is allowed in drinking water. MCLs are set as close to the health goals as possible, considering cost, benefits and the ability of public water systems to detect and remove contaminants using suitable treatment technologies (USEPA, 2009) The MCLs for benzene, toluene, and xylene are listed in the Table 37.

Table 37 MCLs of benzene, toluene, and xylene (USEPA, 2009)

Contaminant	MCL (mg/m ³)
Benzene	5
Toluene	1000
Xylene	10000

According to the corresponding equation and parameters assumed in scenario #3, the limit intakes for benzene, toluene, xylene, and butane by ingestion can be calculated. The results are shown in Table 38.

Table 38 Limit intakes of benzene, toluene, and xylene in drinking water

Contaminant	Limit intake (mg/kg-day)
Benzene	6.12E-05
Toluene	0.029
Xylene	0.286

For OPAL, based on the results from Table 30, the intake of benzene by ingestion drinking water contaminated with OPAL is lower than the limit values. This is also the case for toluene, and xylene. Therefore, the exposure risk for an individual by ingestion drinking water contaminated with OPAL is also practically negligible. Moreover, through comparison OPAL has less risk than that of ULP in this scenario.

Based on the results from the five scenarios, the exposure risks by using OPAL meet the corresponding standards, which means that the exposure risks to human health by using OPAL can be regarded as practically negligible. Moreover, through comparison it is obvious that OPAL has less risk than ULP in all five scenarios, which means OPAL is safer to human health than ULP.

Chapter 6 Conclusion

To reduce the adverse impacts on human health by gasoline sniffing in remote areas, OPAL is thought to be a good option. However, no existing information was found focused on estimating the environmental and human health risks and impacts of OPAL. Therefore, risk-based life cycle analysis and human health risk assessment were conducted to estimate the environmental and human health performance of OPAL, and its comparison to ULP.

Through the life cycle assessment, OPAL was identified to have less adverse impacts on both the environment and human health. However, the risk to human health caused by OPAL remained unknown. Therefore, a human health risk assessment was also conducted. The results showed that the risks to human health by using OPAL can be regarded as negligible. Moreover, compared to ULP, OPAL has less risk in all five scenarios.

In summary, it may be concluded that in contrast to ULP, OPAL causes much less adverse impacts on the environment and human health and has negligible risk to human health. In contraction of above conclusions, it can be predicted that introduction of OPAL to remote areas will significantly reduce the harmful effects caused by gasoline sniffing.

However, since a lack of information and data, there are some uncertainties in this study. Therefore, some recommendations are suggested in order to improve this study. Although a general uncertainty analysis was conducted in order to indicate that these uncertainties would not change the overall conclusion, it would be better to quantifying the uncertainty instead of purely doing a qualitative uncertainty analysis.

In addition, another expectation in such case study is that the study can contribute back to the methodology. This study may help to point to some limitations of the methodology or suggest some modifications to the methodology.

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